anti-reflect
outer surface
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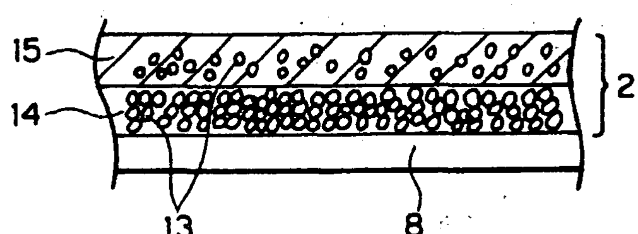
(54) Conductive anti-reflection film and cathode ray tube

(57) A conductive anti-reflection film (2) comprises a first layer containing first conductive particles and a second layer covering the first layer, the second layer containing SiO_2 and second conductive particles. such a conductive anti-reflection film prevents or minimises occurrence of AEF (Alternating Electric Field) and light from reflecting and allows the front surface to be conductive. In addition, the conductive anti-reflection film permits high productivity with high durability. A cathode ray tube whose external surface is coated with such film can display a high quality picture during a long service life.

FIG. 1B

SiO2



conductive

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Description

The present invention is concerned with conductive anti-reflection films that functions as an anti-reflection film which also prevents occurrence of AEF (Alternative Electric Field). The invention also concerns a cathode ray tube that suppresses light from reflecting on an outer surface of a face panel and thereby substantially or completely prevents the AEF from taking place.

An electron gun and a deflection yoke of a cathode ray tube such as a TV Braun tube, a computer monitor, or the like generate electromagnetic waves.

The possibility of such electromagnetic waves which leak out from a cathode ray tube adversely affecting adjacent electronic devices has been suggested.

To preventthese electromagnetic waves (electric field) of a cathode ray tube from leaking out, a method for decreasing the surface resistance of the face panel of the cathode ray tube has been proposed.

For example, Japanese Patent Laid-Open Application Nos. 61-118932, 61-118946, and 63-160140 disclose various surface treatment methods for preventing a face panel from being charged. With these methods, the AEF has been prevented. As methods for forming a conductive layer with a low surface resistance on a face panel, gas phase methods such as PVD method, CVD method, and spattering are known. For example, Japanese Patent Laid-Open Application No. 1-242769 discloses a method for forming a transparent low-resistance conductive layer using a spattering method.

Generally, the refractive index of a conductive layer is high. Thus, it is difficult to have sufficient anti-reflection effect with only a conductive layer. Consequently, to satisfy both properties of conductivity and anti-reflection and to protect a conductive layer, the conductive layer of the conductive anti-reflection film is covered with an anti-reflection layer containing SiO_2 and having a low refractive index. However, the surface resistance of the anti-reflection layer that contains SiO_2 and has a low refractive index is high. When the conductive layer is covered with the anti-reflection layer, the anti-reflection layer does not have conductivity.

To allow an anti-reflection layer of a cathode ray tube to be conductive, the following structures have been proposed.

(1) To allow a conductive layer 3 as part of a conductive anti-reflection film 2 formed on a face panel 8 to be conductive, a conductor portion 5 that pierces the anti-reflection layer 4 and contacts the conductor layer 3 is formed. Thereafter, the conductor portion 5 is filled with a special solder 6 (see Fig. 2).

(2) An area for a conductor portion 5 is formed in a conductor layer 3. An anti-reflection layer 4 is not formed in the conductor portion 5 (see Fig. 3).

(3) An anti-reflection layer 4 that is a porous layer is covered on a conductive layer 3. A part of the conductive layer 3 is exposed as a conductive portion.(see Fig 4)

However, when a conductive portion that pierces an anti-reflection layer is formed so as to allow a conductive anti-reflection film to be conductive and the conductive portion is filled with solder, the structure of the conductive anti-reflection film becomes complicated. In addition, since the number of fabrication steps increases, the productivity of the conductive anti-reflection film decreases.

On the other hand, when a conductive layer is covered with an anti-reflection layer that is a porous layer, the strength of the anti-reflection layer decreases. Thus, the durability of the conductive anti-reflection film decreases significantly.

In a method for forming a conductive layer on a substrate such as a face panel, a solution in which conductive oxide particles or metal particles have been dispersed is coated on a substrate by a coating method or wetting method. The resultant coated film is dried or baked and thereby a conductive layer is obtained.

In this method, a plurality of layers are formed on the substrate whereby the refractive index of an inner layer of (adjacent to) the substrate is higher than the refractive index of an outer layer of (apart from) the substrate. In other words, the refractive index of the outermost layer is the lowest.

However, since the refractive index of a layer with higher conductivity is higher than the refractive index of a layer with lower conductivity, when a conductive layer is formed as an outermost layer disposed against the substrate, the characteristic for protecting the conductive anti-reflection film from reflecting light deteriorates or vanishes.

An anti-reflection layer that contains SiO_2 and that has a low refractive index is formed on a conductive layer so as to prevent light from reflecting. In this case, the anti-reflection layer functions as a capacitor. Thus, the surface resistance of the conductive anti-reflection film cannot be sufficiently decreased. Consequently, a conductive portion cannot be formed on the front surface of the conductive anti-reflection film.

An object of the present invention is to provide a conductive anti-reflection film that substantially or completely prevents the AEF (Alternating Electric Field) from taking place and light from reflecting and, allows the front surface thereof to be conductive, and has high productivity and durability.

Another object of the present invention is to provide a cathode ray tube that has such a conductive anti-reflection

film and that can display a high quality picture for a long service life.

According to the present invention, a layer of the front surface (an outermost layer against the substrate) of a conductive anti-reflection film contains SiO_2 and conductive particles so as to allow the front surface thereof to be conductive. Thus, a conductive portion can be easily formed on the front surface of the conductive anti-reflection film

A first aspect of the present invention is a conductive anti-reflection film, comprising a first layer containing first conductive particles, and a second layer disposed for covering the first layer, the second layer containing SiO_2 and second conductive particles.

According to the conductive anti-reflection film of the present invention, the first layer containing conductive particles is covered with the second layer containing SiO_2 and conductive particles. Thus, the refractive index of the second layer becomes smaller than the refractive index of the first layer. In addition, the surface resistance of the second layer can be decreased. Thus, the second layer prevents light from reflecting. In addition, a conductive portion can be disposed on the second layer.

A second aspect of the present invention is a cathode ray tube, comprising a face plate having a first surface containing a phosphor substance, a first layer disposed on a second surface opposite to the first surface of the face plate, the first layer containing first conductive particles, and a second layer disposed for covering the first layer, the second layer containing SiO_2 and second conductive particles.

According to the cathode ray tube of the present invention, the first layer containing conductive particles is disposed on the second surface opposite to the first surface containing a phosphor substance. The first layer is covered with the second layer containing SiO_2 and conductive particles. Thus, the refractive index of the second layer becomes smaller than the refractive index of the first layer. In addition, the surface resistance of the second layer can be decreased. Consequently, the second layer can prevent light from reflecting and electrically contact with desired conductivity.

The conductive particles contained in the first layer may be the same as or different from the conductive particles contained in the second layer.

Examples of the conductive particles used in the present invention are super fine particles of at least one substance selected from the group consisting of gold, silver, silver compound, copper, copper compound, tin compound, and titanium compound. Examples of the silver compound are silver oxide, sliver nitrate, silver acetate, silver benzoic acid, ~~silver bromate, silver~~ bromide, silver carbonate, silver chloride, silver chromate, silver citric acid, and silver cyclohexane butyric acid. To allow the silver compound to be more stably present in the first layer and the second layer, preferable examples of the silver compound are Ag-Pd, Ag-Pt, and Ag-Au. Examples of the copper compound are copper sulfate, copper nitrate, and copper phthalocyanine. Examples of the tin compound are ATO (antimony tin oxide) and ITO (Indium tin oxide) such as $Sb_xSn_{1-x}O_2$ and $In_xSn_{1-x}O_2$. An example of the titanium compound is TiN.

The conductive particles are those of at least one of the above-described substances.

The larger the diameter of conductive particles, the higher the conductivity. However, to improve the optical characteristics of the conductive anti-reflection film, the diameter of the particles is preferably 400 nm or less, more preferably, 50 to 200 nm (in this case, the diameter of particles represents the diameter of a sphere with the same volume of each particle). When the diameter of the conductive particles exceeds 400 nm, the transmissivity of light of the conductive anti-reflection film significantly deteriorates. In addition, since the particles cause light to scatter, the conductive anti-reflection film gets dimmed. On the other hand, when a conductive anti-reflection film containing conductive particles whose diameter exceeds 400 nm is used for a cathode ray tube, the resolution thereof may deteriorate.

The content of the conductive particles contained in the second layer is preferably 5 to 50 wt %, more preferably 10 to 40 wt % based on the total content by weight of SiO_2 (namely, conductive particles (wt) / SiO_2 (wt) x 100). When the content of the conductive particles contained in the second layer is 5 wt % or less (based on the total content by weight of SiO_2), the surface resistance of the second layer may not be a low resistance value that allows the second layer to be conductive as the front surface of the conductive anti-reflection film.

When the content of the conductive particles contained in the second layer exceeds 50 wt % (based on the total content by weight of SiO_2), the reflectivity of light of the conductive anti-reflection film becomes high. Thus, the conductive anti-reflection film may not sufficiently protect light from reflecting.

In addition, according to the present invention, to improve the optical characteristic of the conductive anti-reflection film, super fine particles of a pigment made of such as copper phthalocyanine may be contained in the first layer. At this point, the diameter of super fine particles is in the range from 10 to 200 nm (in this case, the diameter of particles represents the diameter of a sphere with the same volume of each particle). In addition, to improve the water resistance, chemical resistance, and so forth of the second layer and thereby improve the reliability of the conductive anti-reflection film, at least one of compounds such as ZrO_2, silane fluoride, and silicate may be contained corresponding to the environmental conditions. Such a compound is contained in the second layer in such a manner that the compound does not adversely affect the characteristic of the conductive anti-reflection film. When ZrO_2 is contained in the second layer, the content of ZrO_2 is preferably 5 to 40 mole %, more preferably, 10 to 20 mole % based on the total molar content of SiO_2 (namely, ZrO_2 (mole) / SiO_2 (mole) x 100). When the content of ZrO_2 in the second layer is less than

multiple metals

5 mole % based on the total molar content of SiO_2, the effect of ZrO_2 is unlikely to be significant. On the other hand, when the content of ZrO_2 contained in the second layer exceeds 40 mole % based on the total molar content of SiO_2, the strength of the second layer deteriorates. In addition, as described above, ZrO_2 may be contained in the second layer along with silane fluoride. In this case, the front surface of the conductive anti-reflection film can have desired conductivity. In addition, the water resistance, acid resistance, alkali resistance, and so forth of the conductive anti-reflection film can be further improved.

According to the present invention, to form the first layer, a solution in which particles of Au, Cu, or the like have been dispersed along with a non-ionic interface activating agent is coated on a substrate that is the outer surface of a face panel of a cathode ray tube by for example spin coating method, spraying method, or dipping method. At this point, to further suppress the first layer from becoming uneven, the temperature of the surface of the substrate is preferably in the range from 5 to 60°C. The thickness of the first layer can be easily controlled by adjusting the concentration of metal particles of Ag and Cu, the number of rotations of a coater used in the spin coating method, the discharging amount of a dispersion solution in the spraying method, and the raising speed in the dipping method. As a solvent of the solution, when necessary, ethanol, IPA, or the like may be contained along with water. In addition, an organic metal compound, a pigment, a dye, or the like may be contained in the solution so as to add another characteristic to the first layer.

As a method for forming the second layer on the first layer, a solution in which particles of Au, Cu, or the like have been dispersed along with a non-ionic interface activating agent is coated on the first layer by for example spin coating method, spraying method, or dipping method. The thickness of the second layer can be easily controlled by adjusting the concentration of metal particles of Ag, Cu, silicate, or the like, the number of rotations of a coater used in the spin coating met-hod, the discharging amount of a dispersion solution in the spraying method, and the raising speed in the dipping method. By simultaneously baking the first coated film and the second coating film at a temperature from 150 to 450°C for 10 to 180 minutes, the conductive anti-reflection film according to the present invention can be obtained. In addition, according to the present invention, to effectively decrease the reflectivity of the conductive anti-reflection film, a third layer may be disposed between the first layer and the second layer, the reflectivity of the third layer preferably being between or almost the middle of the reflectivity of the first layer and the reflectivity of the second layer. In other words, the conductive anti-reflection film may be composed of two or more layers. At this point, when the difference of the refractive indexes of two adjacent layers is small, the reflectivity of the conductive anti-reflection film can be effectively decreased. According to the present invention, when the conductive anti-reflection film is composed of the first layer and the second layer, the thickness and refractive index of the first layer is preferably 200 nm or less and preferably 1.7 to 3, respectively. The thickness and refractive index of the second layer is preferably 10 times or less and preferably 1.38 to 1.70 times as large as those of the first layer, respectively. When the third layer is disposed between the first layer and the second layer, the thickness and refractive index of each of the first to third layers may depend on or be selected according to the transmissivity and refractive index of the conductive anti-reflection film.

In order that the invention may be illustrated, more easily appreciated and readily carried into effect by those skilled in the art, embodiments of the invention will now be described purely by way of non-limiting example with reference to the accompanying drawings Figures 1A and 1B and prior art drawings Figures 2 to 4 wherein:

Fig. 1A is a perspective partial cut-away view showing the structure of a cathode ray tube according to the present invention;
Fig. 1B is a sectional view taken along line A - A' of the cathode ray tube shown in Fig. 1A;
Fig. 2 is a sectional view showing the structure of a conductive anti-reflection film of a conventional cathode ray tube;
Fig. 3 is a sectional view showing the structure of a conductive anti-reflection film of a conventional cathode ray tube; and
Fig. 4 is a sectional view showing the structure of a conductive anti-reflection film of a conventional cathode ray tube.

Particles of ITO (Indium tin oxide) were dispersed in ethanol. Thus, a dispersed solution of 2 wt % of ITO was obtained. Particles of ITO were added and mixed to a solution of 1 wt % of silicate (a solution of mixed composition of trimer and tetramer of tetramethoxysilane (the degree of polymerization is 3.5 (average)) so that the solid component of SiO_2 to the solution of 1 wt % of silicate becomes 0 wt % (comparative example), 5, 10, 20, 40, 50, and 100 wt % (first to sixth embodiments). Thus, second to sixth dispersed solutions were obtained. In this example wt % represents ITO (wt) / SiO_2 (wt) x 100.

Next, the outer surface of a face panel (17-inch panel) of a cathode ray tube that had been assembled was buffed with cerium oxide. After rubbish, dust, and oil were removed from the buffed surface, the first dispersed solution was coated on the buffed surface by the spin coating method. Thus, a first film was formed. The coating conditions of the first film were in the following conditions.

Panel temperature (coated surface): 30°C

Number of rotations of coater in solution pouring stage: 80 rpm - 5 sec
Number of rotations of coater in solution shaking stage (film forming stage): 150 rpm - 80 sec

Next, the second to eighth solutions were coated on the first film by the spin coating method in the following conditions.

Number of rotations of coater in solution pouring stage: 80 rpm - 5 sec
Number of rotations of coater in solution shaking stage: 150 rpm - 80 sec

Thereafter, the first film and the second film were baked at a temperature of 210°C for 30 minutes.

Fig. 1A and 1B show a cathode ray tube according to the first to sixth embodiments of the present invention.

In Fig. 1A, a color cathode ray tube has a panel 1 and an enclosure. The enclosure is composed of a funnel integrally connected to the panel 1. Inside a face panel 8 assembled to the panel 1, a phosphor surface 9 is formed. The phosphor surface 9 is composed of a three-color phosphor layer and a black-light-absorbing layer. The three-color phosphor layer emits rays of blue, green, and red. The black light absorbing layer is disposed in the space of the three-color phosphor layer. The three-color phosphor layer is obtained in a conventional method for example by coating a slurry of which each color phosphor has been dispersed in PVA, surface activating agent, and demineralized water on the inner surface of the face panel 8. The three-color phosphor layer may be formed in a stripe shape or in a dot shape. In this example, the three-color phosphor layer is formed in a dot shape. A shadow mask 10 having many electron beam holes is disposed opposite to the phosphor surface 9. An electron gun 12 is disposed in a neck 11 of the funnel 7. The electron gun 12 emits an electron beam to the phosphor surface 8. The electron beam emitted from the electron gun 12 hits the phosphor surface 9 and thereby excites the three-color phosphor layer. Thus, rays of three colors are emitted. A conductive anti-reflection film 2 is formed on the outer surface of the face panel 8. Fig. 1B is a sectional view taken along line A - A' of the cathode ray tube shown in Fig. 1A. On the front surface of the face panel 8, the conductive anti-reflection film 2 is formed. The conductive anti-reflection film 2 is composed of a first layer (conductive layer) 14 and a second layer 15. The first layer 14 contains particles 13 of ITO. The second layer 15 is composed by dispersing particles 13 of ITO within a matrix of SiO_2.

For each of the conductive anti-reflection films obtained as the first to sixth embodiments and the comparative example, the surface resistance, the resistance stability, the film strength, and the visible regular reflectivity were measured. The surface resistance was measured with Loresta IP MCP-T250 (made by Yuka Denshi). With respect to the resistance stability, variations of measured values were examined (in Table 1, O represents absence of variation, whereas X represents presence of variation). With respect to the film strength, a probe composed of SUS 304 was contacted to each of the individual respective conductive anti-reflection films at a pressure of 1.5 kg/cm^2. Thereafter, with the pressure of 1.5 kg/cm^2 of the probe, each of the conductive anti-reflection films was moved. (In Table 1, a conductive anti-reflection film that was not scratched by the probe is denoted by O, whereas a conductive anti-reflection film that was scratched by the probe is denoted by X). The visible regular reflectivity was measured by CR-353G (made by Minoruta). Table 1 lists the measured results of the conductive anti-reflection films according to the compared example and the first to sixth embodiments.

Table 1

	Comparative Example	First Embodiment	Second Embodiment	Third Embodiment	Fourth Embodiment	Fifth Embodiment	Sixth Embodiment
Added content of ITO (Ratio to SiO_2: wt %)	0	5	10	20	40	50	100
Surface resistance	16-21	4	0.45	0.36	0.30	0.30	0.28
Resistance stability	×	○	○	○	○	○	○
Film strength (scratch test)	○	○	○	○	○	○	×
Visible regular reflectivity	1.4	1.5	1.6	1.7	2.0	2.5	3.0

As is clear from Table 1, since the front surface of each of the conductive anti-reflection films according to the first to sixth embodiments has conductivity, the surface resistance thereof is low and the resistance stability thereof is sufficient. In addition, the visible reflectivity is sufficient. On the other hand, since the second layer of the conductive anti-reflection film according to the compared example does not contain particles of ITO, the surface resistance is high and the resistance stability is insufficient. As a result, the front surface of the conductive anti-reflection film according to the compared example does not have conductivity.

In the sixth embodiment, although the film strength is denoted by X, the film strength of the conductive anti-reflection film is practically sufficient.

As is clear from the above-described embodiments, according to the conductive anti-reflection films of the present invention, the first layer containing the first conductive particles is covered with the second layer of which the second conductive particles are contained in the matrix of SiO_2. Thus, the refractive index of the second layer becomes smaller than the refractive index of the first layer. In addition, the surface resistance of the second layer can be decreased. Thus, a conductive anti-reflection film that prevents the AEF from taking place, that prevents light from reflecting on the second layer, and that allows the second layer to be conductive can be provided. In addition, since the conductive anti-reflection film is conductive, another conductive means is not required. Thus, the productivity of the conductive anti-reflection film is high. Moreover, since the stability of the second layer that covers the first layer is high, a conductive anti-reflection film with high durability can be provided.

In addition, according to a cathode ray tube of the present invention, since the first layer containing the first conductive particles is disposed on the surface of the face plate, the first layer is covered with the second layer containing SiO_2 and the second conductive particles. Thus, the refractive index of the second layer becomes smaller than the refractive index of the first layer. In addition, the surface resistance of the second layer can be decreased. Thus, a cathode ray tube that prevents the AEF (Alternating Electric Field) from taking place, that prevents light from reflecting on the second layer, and that allows the second layer to be stably conductive without need to form a conductive portion can be provided. In addition, with the conductive anti-reflection film, another conductive means is not required. Thus, a cathode ray tube with high productivity can be provided. In addition, since the stability of the second layer that covers the first layer is high, a cathode ray tube that can display a high quality picture for a long service life can be provided.

Claims

1. A conductive anti-reflection film, comprising:

   a first layer containing first conductive particles; and
   a second layer disposed to cover said first layer, said second layer containing SiO_2 and second conductive particles.

2. A conductive anti-reflection film as claimed in claim 1,
   wherein the first conductive particles and the second conductive particles are the same material or different materials selected from the group consisting of gold, silver, silver compound, copper, copper compound, tin compound, and titanium compound.

3. A conductive anti-reflection film as claimed in claim 1 or 2,
   wherein the diameter of the first and second particles is 400 nm or less (the diameter of particles represents the diameter of a sphere with the same volume of each particle).

4. A conductive anti-reflection film as claimed in any preceding claim,
   wherein the content of the second conductive particles contained in said second layer is in the range from 5 to 50 wt % to the total content of the second particles and SiO_2.

5. A conductive anti-reflective film as claimed in any preceding claim wherein the first layer further contains superfine pigment particles.

6. A film as claimed in any preceding claim wherein said pigment comprises a copper compound.

7. A film as claimed in any preceding claim wherein the second layer further contains one or more of: ZrO_2, silane fluoride and silicate. oxide a silicate

8. A film as claimed in any preceding claim further comprising a third layer interposed between said first and second

layers.

9. A film as claimed in claim 8 wherein the reflectivity of said third layer lies between the reflectivity of said first and second layers.

10. A cathode ray tube, comprising:

    a face plate having a first surface containing a phosphor substance; and
    a film disposed on a second surface opposite to the first surface of said face plate, said film comprising a conductive anti-reflection film as claimed in any preceding claim, wherein said first layer is in contact with said second surface.

11. A method of making a film-coated cathode ray tube as defined in claim 10 which comprises applying to said second surface a first layer as defined in any one of claims 1 to 9 and causing or allowing said layer to set or harden, followed by application to said set or hardened first layer a second layer as defined in any one of claims 1 to 9 and causing or allowing said second layer to set or harden.

FIG. 1A

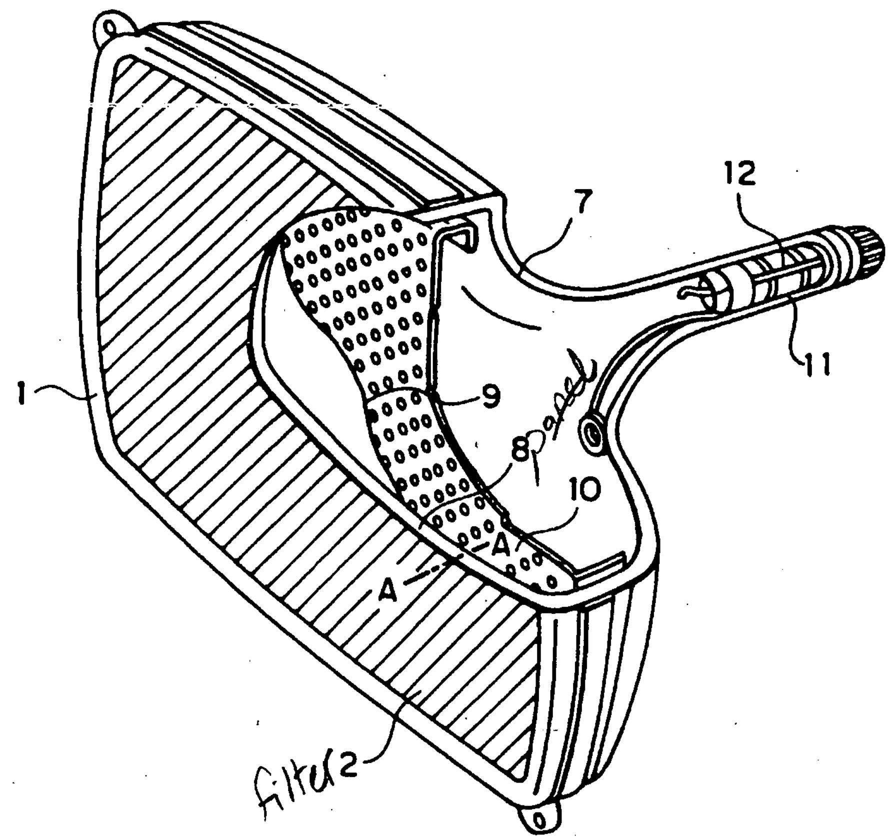


FIG. 1B

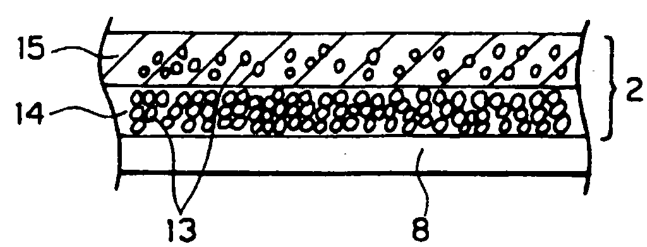


FIG. 2

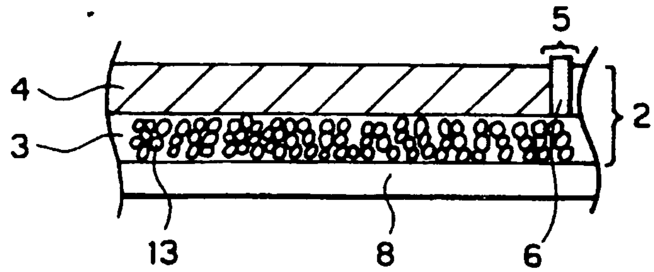


FIG. 3

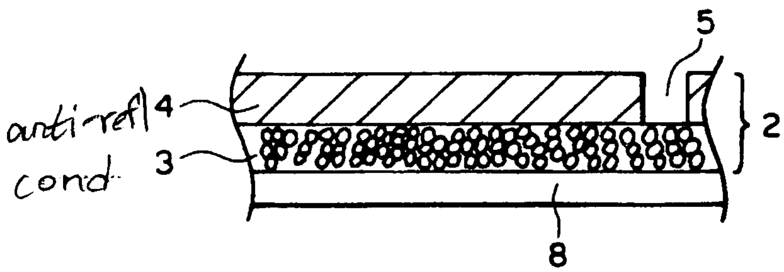
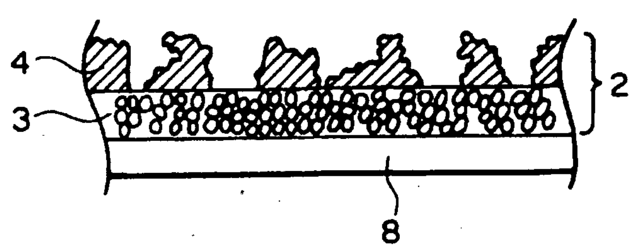


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 5424

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 412 278 A (IWASAKI YASUO) 2 May 1995 * column 3, line 30 - line 65 * * column 4, line 5 - line 34 * * column 5, line 11 - line 27 * ---	1,2,5, 8-11	H01J29/86 H01J29/89
X	US 5 346 721 A (TONG HUA-SOU ET AL) 13 September 1994 * column 1, line 33 - line 50 * ---	1-3,10, 11	
X	US 5 243 255 A (IWASAKI YASUO) 7 September 1993 * column 9, line 66 - column 12, line 7 * ---	1-3,5, 9-11	
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 007, 31 July 1997 -& JP 09 076401 A (MITSUBISHI MATERIALS CORP), 25 March 1997 * abstract * ---	1-5,10	
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 203 (E-1354), 21 April 1993 & JP 04 345737 A (MITSUBISHI ELECTRIC CORP), 1 December 1992 * abstract * ---	1,5,10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01J
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 002, 29 February 1996 & JP 07 282745 A (COLCOAT KK), 27 October 1995 * abstract * -----	1-4,10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 October 1998	Colvin, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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